

1 **METHOD FOR ANNEALING AN ELECTRODEPOSITION STRUCTURE**

2 FIELD OF THE INVENTION

3 This invention relates to a method for annealing electrodeposition structures
4 formed by electrodeposition techniques particularly suitable for use in electroforming.

5 BACKGROUND OF THE INVENTION

6 U.S. Patent No. 4,623,503 to Anestis et al. entitled "Slush Molding Method With
7 Selective Heating of Mold By Air Jets", assigned to the assignee of the present invention
8 and hereby incorporated by reference, discloses a method of slush molding with the use
9 of an electroformed nickel mold.

10 According to U.S. Patent No. 4,108,740 to Wearmouth entitled "Hard, Heat-
11 Resistant Nickel Electrodeposits", the production of electroforms involves building up
12 deposits of adequate thickness on a mandrel without internal stress in the deposit so high
13 as to cause premature separation of the deposit from the mandrel. The '740 Patent goes
14 on to state that the electroformability and hardness of nickel can be improved by
15 electrodepositing the nickel from an electrolyte containing addition agents which
16 introduce sulfur into the resulting electrodeposit and that, while sulfur improves
17 electroformability by reducing the internal stress in the electrodeposit, it does so at the
18 expense of ductility. In the '740 Patent, for example, it is reported that sulfur contents in
19 excess of approximately 0.005% cause the electrodeposit to embrittle upon exposure to
20 temperatures above about 200 degrees Celsius, and that embrittlement at temperatures
21 above ambient is particularly disadvantageous in electroforms requiring exposure to
22 elevated temperatures, in applications such as molds and dies, or in fabrication such as

1 screen printing cylinders which can be subjected to localized heating by brazing, welding
2 or by the use of heat curable glues, or during surface masking using heat curable
3 lacquers.

4 According to U.S. Patent No. 5,470,651 to Milinkovic et al. entitled "Mandrel For
5 Use in Nickel Vapor Deposition Processes And Nickel Molds Made Therefrom" one
6 drawback of electroformed nickel shells and molds, in consequence of the fact that
7 electroformed nickel contains relatively large amounts of sulphur, is that repairs or
8 modifications to the shell or mold by means of welding cannot be preformed readily.

9 In addition to the above drawbacks, the Applicant has found that electrodeposition
10 structures, such as the electroformed molds discussed above, may contain voids within
11 the electrodeposition structure itself. These voids are formed during the build-up of
12 deposits on the mandrel and are ordinarily of microscopic size, generally round in shape
13 and on the magnitude of less than 0.005" in size.

14 Applicant has also found that, during heating of the electrodeposition structure,
15 these voids, depending on their proximity to the surface of the electrodeposition structure,
16 may cause the surface of the electrodeposition structure to distort in the form of a
17 protuberance, similar to that of a bulge or bump, on the electrodeposition surface.
18 Without being bound to a particular theory, the Applicant believes that heating of the
19 electrodeposition structure causes pressure from gas, believed to comprise hydrogen
20 generated and entrained during formation of the electrodeposition structure, within the
21 void to increase. As a result, particularly in those areas of the electrodeposition structure
22 where the voids are nearest the surface, the increase in gas pressure within the void

1 overcomes the bending strength of the thin electrodeposition thickness above the void
2 and forces the surface of the electrodeposition structure to rise.

3 In those instances where the voids produce surface protuberances, the Applicant
4 has found that the voids may be repaired via welding. However, more problematic is
5 whether the texture of the surface of the weld and surrounding electrodeposition structure
6 are uniform and blended as to completely hide the presence of the repair. Applicant has
7 found that the ability to repair the surface of the weld and surrounding electrodeposition
8 structure adequately depends largely on the texture of the surface of the electrodeposition
9 structure. Many of the electroformed molds used in the automotive industry have a grain
10 texture formed on the electrodeposition surface. In some instances the texture of the
11 electrodeposition surface can be repaired, while in other instances it cannot be
12 successfully repaired as the grain pattern cannot be replicated in the repaired area. Thus,
13 at the very least, voids in the electrodeposition structure result in costly repairs and time
14 and, on occasion, the complete electrodeposition structure becomes scrap.

15 Furthermore, Applicant believes that while certain of the voids contained within
16 the electrodeposition structure may not produce protuberances on the surface of the
17 electrodeposition structure in response to heating of the structure, nevertheless Applicant
18 believes these voids may weaken the overall electrodeposition structure resulting in
19 premature cracks, metal fatigue, etc. of the electrodeposition structure.

20 What is needed is a process to anneal an electrodeposition structure to make the
21 structure more ductile so as make the structure more receptive to repairs or modifications
22 by means of welding. What is also needed is a process to anneal the electrodeposition

1 structure such that the likelihood of voids which may be formed in the structure, giving
2 rise to protuberances on the surface of the structure during heating, is reduced and more
3 preferably eliminated.

4 SUMMARY OF THE INVENTION

5 Accordingly, one of the objects of the present invention is to provide a new and
6 improved process for providing electrodeposition structures that have improved grain
7 structure and reduced voids which may cause surface disruption.

8 Another object of the present invention is to provide an electrodeposition
9 structure having greater ductility and a reduced propensity for surface disruption.

10 A further object of the present invention is to provide an annealing process that
11 provides electrodepositon structures that are easier to repair.

12 The above objects and others are realized in accordance with the invention by a
13 method in which an electrodeposition structure is exposed to heat and pressure above
14 ambient to increase the ductility and change the grain structure of the electrodeposit. In
15 one form of the invention, the electrodeposition structure is exposed to and held at a
16 temperature between and including 48 and 99% of the melting temperature of the
17 electrodeposit in an argon gas atmosphere. Upon cooling to ambient, improvements in
18 ductility and grain structure of the electrodeposit were noted.

19 In another form of the present invention, an electrodeposition structure is heated
20 to and held at a temperature between and including 48 and 99% of the melting
21 temperature of the electrodeposit under argon gas at 15,000 psi. Upon returning the

1 structure to ambient conditions, further improvements in ductility and grain structure
2 were noted.

3 In another form of the invention, a method for annealing a structure formed by
4 electrodeposition is disclosed, the method comprising first providing the
5 electrodeposition structure, the electrodeposition structure comprising an electroformed
6 mold, the electroformed mold having a nominal thickness between and including 0.5mm
7 to 8.0mm and having a melting temperature; heating the electrodeposition structure to a
8 temperature between ambient temperature and the melting temperature of the
9 electrodeposition structure; isostatically pressurizing the electrodeposition structure to a
10 pressure above ambient pressure; cooling the electrodeposition structure to ambient
11 temperature; and depressurizing the electrodeposition structure to ambient pressure.

12 In yet another form of the invention, an electroformed mold is disclosed, the
13 electroformed mold annealed at an annealing temperature above ambient temperature and
14 an annealing pressure above ambient pressure wherein the electroformed mold comprises
15 a material having an elongation measured at break before and after annealing, the
16 elongation at break after annealing being greater than the elongation at break before
17 annealing.

18 In yet another form of the invention, an electroformed mold is disclosed, the
19 electroformed mold comprising a material having voids therein, at least a portion of the
20 voids forming at least one protuberance on the surface of the electroformed mold when
21 the mold is exposed to heat wherein the electroformed mold is annealed at an annealing
22 temperature above ambient temperature and an annealing pressure above ambient

1 pressure and wherein the number of voids forming protuberances on the surface of the
2 electroformed mold is reduced after annealing of the electroformed mold as compared to
3 before annealing of the electroformed mold.

4 BRIEF DESCRIPTION OF THE DRAWINGS

5 These and other objects, features and advantages of the invention will become
6 apparent upon consideration of the description of the invention and the appended
7 drawings in which:

8 FIG. 1 is a representative perspective view of an exemplary electrodeposition
9 structure which may be treated after formation in accordance with the present invention;

10 FIG. 2 is a representative cross-sectional view of the electrodeposition structure of
11 FIG. 1 during formation thereof taken along line 2-2;

12 FIG. 3 is a representative perspective view of another exemplary
13 electrodeposition structure which may be treated after formation in accordance with the
14 present invention;

15 FIG. 4 is a stress-strain graph produced from test specimens taken from the
16 electrodeposition structure of FIG. 3 and partially recorded in Table I,

17 FIG. 5 is an enlarged cross-sectional view of the electrodeposition structure of
18 FIG. 3 taken in the direction of line 3-3 and magnified 100x without any annealing after
19 formation;

20 FIG. 6 is an enlarged cross-sectional view of the electrodeposition structure of
21 FIG. 3 taken in the direction of line 3-3 and magnified 100x after treatment in accordance
22 with Annealing Process No. 1 of the present invention;

1 FIG. 7 is an enlarged cross-sectional view of the electrodeposition structure of
2 FIG. 3 taken in the direction of line 3-3 and magnified 100x after treatment in accordance
3 with Annealing Process No. 2 of the present invention;

4 The above and other objects, feature, and advantages of the present invention will
5 be apparent in the following detailed description thereof when read in conjunction with
6 the appended drawings wherein the same reference characters denote the same or similar
7 parts throughout the several views.

8 DESCRIPTION OF THE INVENTION

9 As used herein, the term "electrodeposition" means the precipitation of a material
10 at an electrode as the result of the passage of an electric current through a solution or
11 suspension of the material, and encompasses both electroforming and electroplating.

12 As used in herein, the term "electrodeposition structure" means a structure
13 produced by electrodeposition.

14 As used herein, the term "electroforming" means the precipitation of material on a
15 mandrel as the result of the passage of an electric current through a solution or
16 suspension of the material, with the mandrel to be separated from the form once the form
17 is completed.

18 As used herein, the term "electroform" means a structure produced by
19 electroforming.

20 In accordance with the invention, an electrodeposition structure, and more
21 specifically an electroform, is shown at 10 in FIG. 1. As shown, electroform 10
22 comprises a thin shell mold comprising nickel and having a nominal thickness in the

1 range between and including 0.5 millimeters to 8.0 millimeters. More preferably, the
2 electroform 10 has a thickness from 2.0 millimeters to 3.5 millimeters. Electroform 10 is
3 preferably used to mold plastic, either thermoplastic or thermoset plastic, by slush,
4 casting or rotational molding techniques as detailed, for example, in U.S. Patent Nos.
5 4,389,177; 4,562,026; 4,610,620; 4,623,503; 4,755,333; 4,780,345; 4,890,995; 4,923,657;
6 4,925,151; 5,032,076; 5,037,678; 5,238,622; 5,290,499; 5,445,510; 5,824,738; and
7 5998,030 assigned to the assignee of the present invention and hereby incorporated by
8 reference.

9 As shown in FIG. 2, electroform 10 is preferably formed via the
10 electrodeposition, and more specifically via electroforming, of nickel onto the surface 12
11 on of a mandrel 14 in a tank 16 containing a solution 18 of nickel sulfamate. However, it
12 should be understood that the present invention is not limited to the electrodeposition of
13 nickel. Other metals can form electrodeposition structures via electrodeposition. Upon
14 reaching the desired thickness, the electroform 10 and mandrel 14 are removed from the
15 tank 16 and separated from one another.

16 As shown in FIG. 3, the geometry of electroform 10 initially selected for
17 annealing and subsequent testing comprises a flat plaque 100. Annealing of electroform
18 100 was then performed under two sets of conditions relative to a control sample upon
19 which no annealing was performed. Measured response variables included tensile
20 strength at 0.2% elongation, tensile strength at break, percent elongation at break and
21 Rockwell B Hardness.

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1 Annealing Process No. 1 (as referenced in FIG. 4) involved heating 3 specimens
2 of electroform 100 in a convection oven under argon gas at atmospheric pressure. The
3 specimens were heated from ambient temperature (i.e. 18-23 degrees Celsius) to 950
4 degrees Fahrenheit (510 degrees Celsius) over a time period of 2 hours. Upon reaching
5 950 degrees Fahrenheit, the specimens of electroform 100 were then maintained at 950
6 degrees Fahrenheit for 4 hours. Thereafter, the specimens were cooled in the
7 convection oven to ambient temperature over a time period of 18 hours.

8 Annealing Process No. 2 (as referenced in FIG. 4) involved heating as well as
9 pressurizing 3 specimens of electroform 100 in a hot isostatic (i.e. uniform) pressure
10 vessel under argon gas at 15,000 psi. (103.4 MPa). The specimens were heated from
11 ambient conditions (i.e. 18-23 degrees Celsius at standard air pressure of 101.3 KPa) to
12 1850 degrees Fahrenheit over a time period of 2 hours. Upon reaching 1850 degrees
13 Fahrenheit (1010 degrees Celsius), the specimens of electroform 100 were then
14 maintained at 1850 degrees Fahrenheit for 4 hours. Thereafter, the specimens were then
15 cooled for 4 hours in the pressure vessel and thereafter removed to cool to ambient
16 temperature.

17 For electroform 100, the melting temperature of the nickel is 2250-2275 degrees
18 Fahrenheit (1232-1246 degrees Celsius). Consequently, for Annealing Process No. 2, the
19 electroform 100 was heated to 81-82% of the melt temperature of the electroform 100.
20 However, heating may be provided in the range between and including 48% to 99% of
21 the melt temperature, or any temperature sufficient to change the "tree ring" nickel
22 laminar structure to a uniform grain structure. Depending on the temperature selected, it

may become necessary to support the electroform 100 in the pressure vessel as to prevent distortion (i.e. sag) of the electroform under its own weight.

With respect to pressure for Annealing Process No. 2, as indicated above, isostatic pressure was maintained at 15,000 psi. However, isostatic pressure may be provided in the range between and including 5000 psi. to 15000 psi., or any pressure sufficient to defuse any entrained nitrogen trapped in the nickel from the plating process and to develop the necessary physical properties.

TABLE I

Specimens	Tensile Strength at 0.2 % Elong.		Tensile Strength at Break		% Elongation at Break	Rockwell B Hardness
<u>Control</u>	<u>KPSI</u>	<u>Mpa</u>	<u>KPSI</u>	<u>MPa</u>		
1	15.1	104.1	74.6	514.3	24.0 %	---
2	29.2	201.3	74.6	514.3	23.5 %	---
3	16.7	115.1	75.1	517.8	25.2 %	---
Mean	20.3	140.2	74.8	515.5	24.2 %	85.3
St. Dev.	7.7	53.2	0.3	2.0	.9 %	1.2
<u>Annealing Process #1</u>						
1	14.9	102.7	54.2	373.7	52.0 %	---
2	10.9	75.2	54.6	376.5	48.4 %	---
3	16.3	112.4	55.5	382.7	48.5 %	---
Mean	14.0	96.3	54.8	377.6	49.6 %	58.0
St. Dev.	2.8	19.3	.7	4.6	2.1 %	1.7
<u>Annealing Process #2</u>						
1	13.4	92.4	49.4	340.6	51.0 %	---
2	9.0	62.1	49.1	338.5	52.0 %	---
3	11.5	79.3	49.4	340.6	54.4 %	---
Mean	11.3	77.9	49.3	339.9	52.5 %	53.0
St. Dev.	2.2	15.2	.2	1.2	1.8 %	1.0

KPSI = Pounds force per square inch x 1000.

Mpa = Megapascals

1 From Table I, it is shown that Annealing Process No. 1 increased the percent
2 elongation at break, and hence the ductility, of the specimens from the electroform 100
3 while correspondingly decreasing the tensile strength at 0.2 percent elongation, tensile
4 strength at break and Rockwell B Hardness.

5 Also from Table I, it is shown that the increased heat and pressure of Annealing
6 Process No. 2 further increased the percent elongation at break of the specimens from the
7 electroform 100 while correspondingly further decreasing the tensile strength at 0.2
8 percent elongation, tensile strength at break and Rockwell B Hardness .

9 In addition to the test data from Table I, FIGS. 5, 6 and 7 are photo-micrographs
10 showing microscopic changes in the cross-sectional structure of electroform 100 in
11 response to the different annealing processes. Turning to the figures, FIG. 5 is an
12 enlarged cross-sectional view of the electroform 100 of FIG. 3 taken in the direction of
13 line 3-3, magnified 100x and with 10% sulfuric acid etch without any annealing after
14 formation. As shown, FIG. 5 clearly shows a structure of distinctly layered deposits
15 throughout the thickness of the structure (somewhat analogous to that of age rings
16 observed on the stump of a tree). As can be seen in FIG. 5, the individual layers are
17 distorted (i.e. wavy) along the length of the cross-section. By comparison, as can be seen
18 in FIG. 6, the distortion of the individual layers along the length of the cross-section is
19 greatly reduced and the interface between the layers is substantially straight. Finally, as
20 can be seen from FIG. 7, the layered disposition of the cross-section of FIG. 5 has given
21 way or changed to a grain structure and the laminar structure is no longer visible.

1 Without being bound to a particular theory, when subjected to high temperature
2 and pressure, a molecular realignment of the nickel occurs. This is very similar to the
3 molecular structure of graphite changing to carbon when graphite is processed using
4 similar temperature and pressure conditions. This is better known as carbon/carbon
5 densification. The end result of processing the nickel under these conditions produces a
6 nickel with greater than 3 times the elongation properties of conventional electroplated
7 nickel. More nickel elongation means the nickel is "tougher" and this is thought to help
8 reduce the nickel tools or molds from cracking.

9 In addition to test data and photomicrographs discussed above, the occurrence of
10 voids that are formed in the electroform and that give rise to protuberances on the surface
11 of the electroform was found to be reduced during subsequent heating to a processing
12 temperature between 162 and 232 degrees Celsius when Annealing Process No. 2 was
13 utilized as compared to when Annealing Process No. 1 or when no annealing process was
14 utilized. Thus, in addition to increasing the percent elongation of electroform 100,
15 Annealing Process No. 2 also decreases the occurrence of surface defects associated with
16 voids within the structure of electroform 100 upon heating of the electroform 100.

17 In other embodiments, the electroform may comprise materials other than nickel.
18 For example, other materials may include, but are not limited to other metals (e.g. copper,
19 silver, gold). Also in other embodiments, the electroform may comprise one or more
20 alloys. Also in other embodiments, the electroform may comprise multiple layers of
21 different materials (e.g. copper and nickel).

1 The description and drawings illustratively set forth our presently preferred
2 invention embodiments. We intend the description and drawings to describe these
3 embodiments and not to limit the scope of the invention. Those skilled in the art will
4 appreciate that still other modifications and variations of the present invention are
5 possible in light of the above teaching while remaining within the scope of the following
6 claims. Therefore, within the scope of the claims, one may practice the invention
7 otherwise than as the description and drawings specifically show and describe.

8